GAS ANALYSIS WITH CARBON MOLECULAR SIEVE

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INTRODUCTION

Carbosieve B is a unique adsorbent for gas solid chromatography which can be used for the separation of:

(1) Permanent gases
(2) Sulfur and nitrogen oxides
(3) Light hydrocarbons C_1 to C_4
(4) Certain lower molecular weight compounds such as formaldehyde, methanol and water
(5) Water from most organics

Because of its inertness it can be used for the determination in the parts per million and parts per billion concentration level. Due to its unique structure, it will elute compounds in an order different from that obtained with other adsorbents or packings.

Carbosieve B is manufactured by SUPELCO, INC. Kaiser[1] described its use for the determination of trace quantities of water and as a general purpose GSC packing[2]. Zlatkis et al. have also described its chromatographic properties for light gas analysis[3].

Carbosieve B is a highly pure carbon with a surface area of approximately $1000 m^2/g$ and pore radius in the range of 10-12 Angstroms, making it essentially a carbon molecular sieve. Its high purity eliminates the adsorption problems that are normally encountered with conventional carbon and other adsorbents; this is an important feature. Its unique surface and structure cause separations which, in many instances, are considerably different from that obtained with other adsorbents.

This adsorbent is highly nonpolar; Rohrschneider Constants show this very well and are as follows:

Benzene (x)	Ethanol (y)	MEK (z)	Nitromethane (u)	Pyridine (s)
-1.03	-0.84	-0.62	-1.93	-1.51

All values are negative indicating that Carbosieve B is even more nonpolar than squalane. Because of its nonpolar character, water is eluted before all organic compounds, even before methane.

APPLICATIONS

PERMANENT GAS SEPARATIONS

Permanent gases such as H_2, O_2, N_2, CO, CH_4 and CO_2 can be separated with Carbosieve B. To do this it is necessary to temperature program the column from room temperature to 175°C. O_2 and N_2 are not easily separated so that a 9 ft. x 1/8" stainless steel column is needed, packed with 120/140 mesh Carbosieve B. The column is held isothermally for four minutes, then programmed at the rate of 30°C/min.

to 175°C. The components are eluted in the order of H_2, O_2, N_2, CO, CH_4 and CO_2. Under these conditions, oxygen and argon are not separated from each other. Figure 3 shows a chromatogram of CO, CH_4 and CO_2 in air.

SEPARATION OF HYDROCARBONS

Carbosieve B can be used to separate hydrocarbons in the C_1 - C_4 range. To do this, the column must be operated above ambient temperature. The C_5 and higher molecular weight hydrocarbons are not eluted from the columns. They appear to be permanently adsorbed by the Carbosieve B. Conceivably they could be eluted if the column temperature were raised sufficiently, but this would result in pyrolysis of the sample. In the C_1 - C_3 range, the compounds are eluted by the degree of unsaturation, with saturated compounds eluted last. This is in contrast to conventional polar columns where the order would be (a) paraffinic (b) olefinic (c) acetylenic. The polar columns would be useful for traces of paraffins in olefins or olefins in acetylenic compounds, but for traces of acetylene in olefins, or olefins in paraffins, Carbosieve B is unique.

C_2 Hydrocarbons

The C_2's are separated in the order acetylene, ethylene and ethane. These components along with methane are shown separated in Figure 4 at 150°C with a 3 ft. x 2mm glass column.

C_3 Hydrocarbons

The C_3's are also separated by the degree of saturation. They are eluted in the order of methylacetylene, allene, propylene, and propane. Cyclopropane and allene are not separated from each other and are eluted together. The separation of the C_3's along with methane and the C_2's is shown in Figure 5 with a 3 ft. column at 200°C.

C_4 Hydrocarbons

In preliminary work with the C_4's, it has been possible to elute iso and n-butane, but not the unsaturated C_4's. The iso and n-butane peaks are relatively broad and are not resolved with a 3 ft. x 2mm column at 275°C. Separation of C_1 - C_4 is shown in Figure 6 at 275°C.

Acetylene in Ethylene

Zlatkis[3] has shown that traces of acetylene can be determined in ethylene. The principal advantage of Carbosieve B for this analysis is that acetylene is eluted before ethylene. This allows a large sample to be used without swamping the acetylene peak, as is the case where ethylene is eluted first.

The separation shown in Figure 2 was carried out with a 3 ft. x 2mm column, Carbosieve B, 45/60 mesh at 140°C, flow 40ml/min. N_2 and a flame ionization detector was used here. Sample size 1.5ml, sensitivity 2 x 10^{-10} A.F.S., 1mv recorder.

SEPARATION OF PERMANENT GASES AND METHANE, ETHYLENE AND ACETYLENE

If it is not necessary to separate O_2 and N_2 but only air, CO, CH_4, CO_2, acetylene, ethylene and ethane, the separation can be carried out with a 4 ft. x 1/8" column with Carbosieve B, 60/80 mesh programmed from 30 to 170°C as shown in Figure 7. If O_2 and N_2 are also to be separated along with CO, CO_2, methane, ethane, ethylene and acetylene, the 9 ft. x 1/8" column used in Figure 3 can be used with the C_2's eluted in order of acetylene, ethylene and ethane.

SEPARATION OF WATER, FORMALDEHYDE AND METHANOL

Kaiser[2] first reported this difficult separation; it can be readily made with Carbosieve B as shown in Figure 1. The separation was made of a formaldehyde solution containing 36-38% formaldehyde, 10% methanol and the remainder water. The conditions used are as follows: Column, 4 ft. x 3mm I.D. glass packed with 60/80 mesh Carbosieve B; Column Temp., 200°C; Flow rate, 75ml/min. Helium: Sample size, 0.5 microliters.

A thermal conductivity detector is used here because it responds to all three components. A flame detector is less suitable since water is not seen at all and formaldehyde only poorly. Note that the order of elution for the three components differs from that obtained with porous polymers.

TRACE ANALYSIS

Trace Gases

Kaiser[2] has shown that trace analysis is possible with Carbosieve B, and that it is possible to detect parts per billion of hydrocarbons using reversion gas chromatography. This technique consists of pulling a large, known volume of the sample through the column, allowing the impurities to collect. Then carrier gas is turned on and the column is heated, by a moving oven, which causes the sample to move through the column. This technique allows for the sample to be highly concentrated in the column.

Since Carbosieve B does not bleed, it can be used with ultra high sensitivity detectors such as helium ionization.

TRACE WATER ANALYSIS

Kaiser[1] has shown that trace quantities of water can be determined using a Carbosieve B column. Because of the low affinity for water of its carbon surface, water is quickly eluted from a Carbosieve B column without tailing even before methane. To carry out trace water analysis, care must be taken to prevent water from being adsorbed on the wall of the column tube. Kaiser has shown that quartz is less adsorptive than glass or stainless steel tubing

SULFUR GASES

Sulfur dioxide is readily eluted from Carbosieve B columns without indication of tailing as shown in Figure 8. Kaiser[4] has found that SO_2 can be determined down to 30 ppm. Below that level the SO_2 is lost on the column. Consequently, Carbosieve B can be recommended only for higher concentrations of SO_2. Hydrogen sulfide tails badly at relatively high concentration so Carbosieve B cannot be recommended for H_2S analysis at this time.

OXIDES OF NITROGEN

Both nitrous oxide (N_2O) and nitric oxide (NO) can be separated from each other as well as other gases with Carbosieve B. No information of nitrogen dioxide (NO_2) is available as yet.

Nitrous oxide is readily separated from other compounds and is eluted after CO_2 and before acetylene. Figure 9 shows N_2O separated from air, methane and CO_2. This separation was carried out at 100°C with a 3 ft. x 1/8" stainless steel column with 60/80 mesh Carbosieve B.

Nitric oxide is eluted from Carbosieve more rapidly than N_2O. At room temperature it is quickly eluted after N_2 and before CO. This is shown in Figure 10 with a 6 ft. x 1/8" stainless steel column with 60/80 mesh Carbosieve B.

Special precautions must be observed when NO is to be separated. The column must be conditioned with hydrogen to prevent the NO peak from tailing. This can be done with either pure hydrogen or a mixed gas such as nitrogen or helium and hydrogen. We have tried a 94% N_2-6% H_2 mixture and found this comparable to pure hydrogen for conditioning. Conditioning for one hour at 200, 300 and 400°C seemed to give essentially the same results. It should be noted that none of the work with NO dealt with trace quantities.

If the column is to be operated at room temperature for NO and then temperature programmed to higher temperatures, the carrier gas should contain hydrogen. If the column is heated without hydrogen in the carrier gas, then the NO peak will tail. This was found with helium as the carrier gas. We found the column gradually deteriorated for NO when the column was repeatedly temperature programmed to 200°C to elute other components. Our work with NO and the hydrogen deactivation has been exploratory, and at this point we are not certain that it can be reproduced.

Both NO and N_2O can be separated from O_2, N_2, CO, CO_2 and methane with a 6 ft. x 1/8" column. The column is operated at room temperature till CO is eluted, then the column is programmed quickly to 150°C to elute methane, CO_2 and N_2O. When the column is programmed, the carrier gas must be dry.

MISCELLANEOUS RETENTION DATA

Data prepared by Kaiser in Table 1 compares Carbosieve B, Porapak Q and Molecular Sieve 5A. Note that the values are retention volumes, not retention times. Water is shown to elute before methane and CO_2 on the Carbosieve B but it is evident that it takes quite some time for butane to be eluted, even at 250°C.

The data in Table 2 were obtained in our laboratory using a 3 ft. x 1/8" O.D. stainless steel column packed with 60/80 Carbosieve B and operated at 40ml/min. and are absolute retention times.

HANDLING OF CARBOSIEVE B

Carbosieve B is supplied in fifteen cc evacuated, sealed vials. When the vial is opened, unused material should be transferred to a glass bottle and tightly closed. To avoid contamination, Carbosieve B should not be exposed to the atmosphere for prolonged periods of time. Because of its high surface area, it tends to readily pick up contaminants from the air; these can be removed but it requires extensive conditioning of the column. To avoid oxidation and damage to its surface, do not heat Carbosieve to over 200°C in air; do not heat columns above this temperature if the carrier gas is not free of oxygen. Columns that are to be temperature programmed should be conditioned for a number of hours at or slightly above the highest temperature anticipated.

Carbosieve B should be used with a carrier gas that is free of oxygen to avoid oxidation of its surface. If oxidation should occur, the peak will show tailing. Oxygen can be removed catalytically by means of specially designed traps which are installed in the carrier gas line.

If temperature programming is used, it is imperative that the carrier gas also be dry. Use of a device such as a molecular sieve trap to remove water is recommended. If the carrier gas is not dry, an irregular base line will be obtained when the column is programmed with a broad peak for water seen in the vicinity of the CO_2

peak. This is a problem with a thermal conductivity detector, but not a flame which does not respond to water.

A drying cartridge should be used to remove water from the carrier gas. One must assume that all carrier gases have some moisture in them. We also find it necessary to install a small drying trap after the flow controller in the instrument. We have seen in several instances where it is the flow controller bleeding moisture that causes the base line problem even though the carrier gas was being dried. One can also heat the carrier gas tubing from the cylinder to the chromatograph to remove moisture from the walls of the tubing, but this is unnecessary if the trap is placed after the controller. A short section of tubing filled with Molecular Sieve 5A is adequate for this. Once this is done, heat the column to the maximum temperature which you expect to reach and hold the column at that temperature for several hours to condition it.

The problem of moisture in the carrier gas is illustrated in Figure 11 which shows the peak for water after CO_2. The size and position of the water peak will depend on the amount of water present.

REFERENCES

(1) Kaiser, R., Chromatographia 2, 453 (1969)
(2) Kaiser, R., Chromatographia 3, 38 (1970)
(3) Zlatkis, A., Kaufman, H. R. and Durbin, D. E., J. Chromatog. Sci. 8, 416 (1970)
(4) Kaiser, R., Private Communication

TABLE 1

	Carbosieve B 150°C	Carbosieve B 250°C	Porapak Q 150°C	Molecular Sieve 5A 150°C	Molecular Sieve 5A 250°C
O_2	1.22	-	0.28	0.32	-
N_2	1.22	-	0.28	0.56	-
CO	1.75	-	0.28	1.34	-
CO_2	9.09	1.80	0.78	43.0	-
CH_4	4.71	1.03	0.40	1.01	-
C_2H_2	21.6	4.08	1.11	-	14.2
C_2H_4	40.5	6.59	1.04	63.9	-
C_2H_6	64.1	9.42	1.23	7.36	-
C_3H_8	-	54.9	3.09	-	47.8
C_4H_{10}	-	126.0	7.83	-	-
C_5H_{12}	-	-	16.72	-	-
CHOH	27.1	3.96	3.78	-	-
CH_3OH	65.7	8.35	5.59	-	-
C_2H_5OH	-	38.3	12.35	-	-
H_2O	4.59	0.51	2.61	-	-

Specific Retention Volume Vg at 150°C

Methane	3.0ml/gm
Ethane	47.4ml/gm
Propane	506.1ml/gm

In the table above (prepared by Kaiser) retention volumes for a number of compounds are compared for several types of columns. In all cases column length was one meter.

TABLE 2

RETENTION TIMES (ABSOLUTE)

	Column Temperature 100°C	150°C	200°C
	Time in Minutes		
H_2	0.23	0.2	0.15
Argon	0.23	0.2	0.15
O_2	0.23	0.2	0.15
N_2	0.23	0.2	0.15
NO	0.23	0.2	0.15
CO	0.23	0.2	0.15
CH_4	0.5	0.3	0.15
CO_2	0.92	0.4	0.27
N_2O	1.45	0.6	0.3
Acetylene	2.4	0.85	0.4
H_2S	4.7	0.450	0.3
Ethylene	5.4	1.6	0.7
Ethane	9.8	2.6	1.0
SO_2	-	5.0	1.6
Methyl Acetylene	-	-	3.7
Cyclopropane	-	12.8	4.2
Allene	-	15.7	4.5
Propylene	-	-	6.0
Propane	-	-	8.6
Water	-	0.15	0.15
Formaldehyde	-	0.35	0.2
Methanol	-	1.0	0.45

Column: 3 ft. x 1/8" S.S., 60/80 mesh Carbosieve B Flow: 40ml/min.

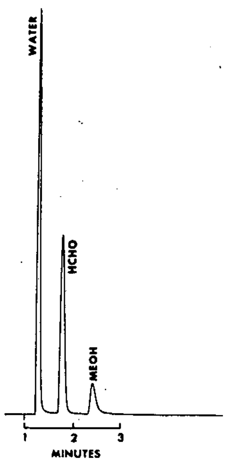

FIGURE 1 – Water-Formaldehyde-Methanol Separation

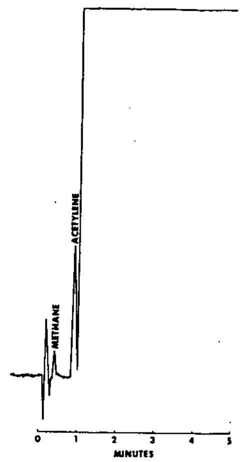

FIGURE 2 – Trace Acetylene in Ethylene

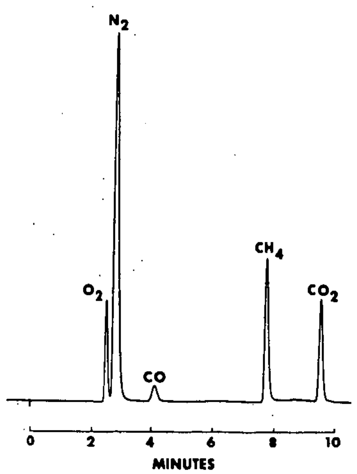

FIGURE 3 – Separation of O_2, N_2, CO, CH_4 and CO_2

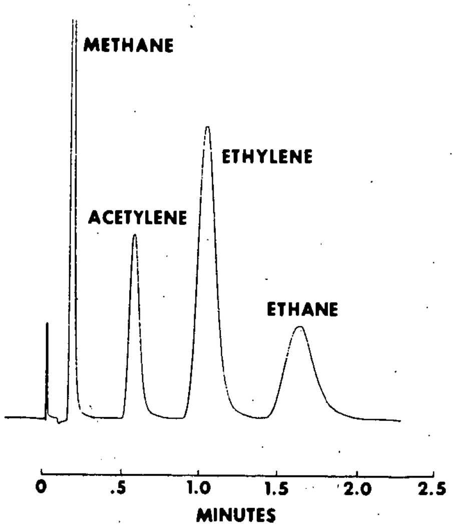

FIGURE 4 – Separation of Methane and C_2's

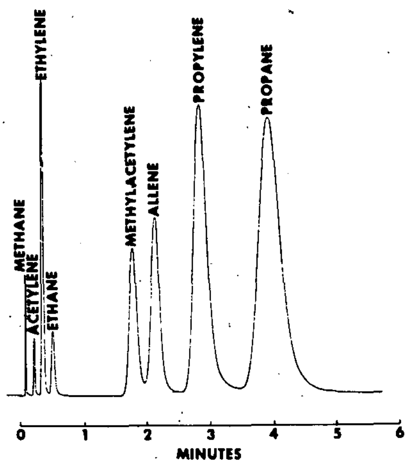

FIGURE 5 – Separation of C_1's, C_2's and C_3's

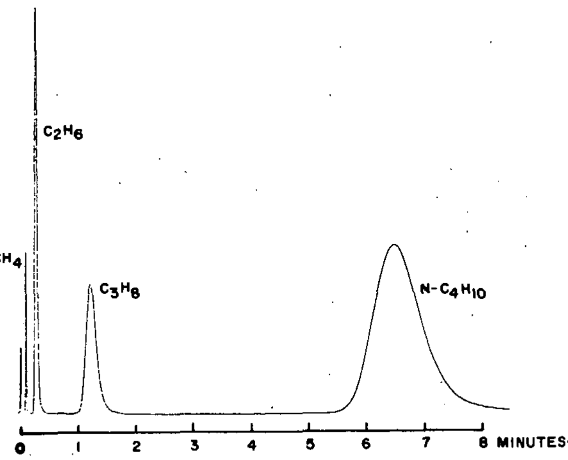

FIGURE 6 – Separation of n-Paraffins - C_1 - C_4

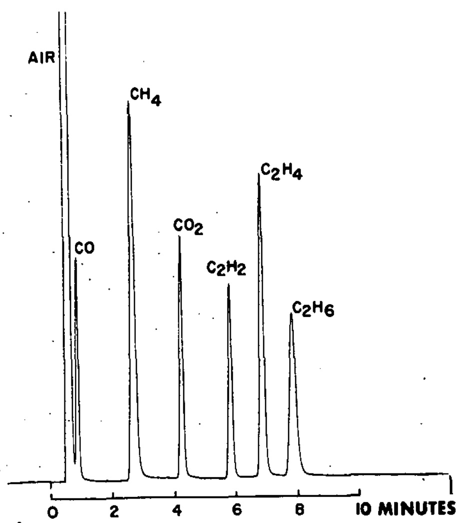

FIGURE 7 – Separation of Air, CO, CH_4, CO_2, C_2H_2, C_2H_4 and C_2H_6

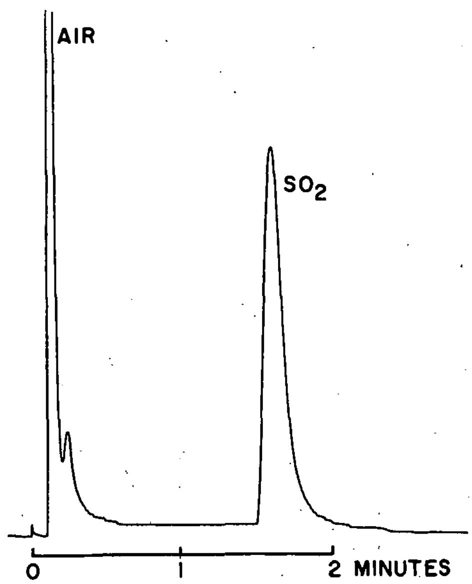

FIGURE 8 – Separation of Air and SO_2

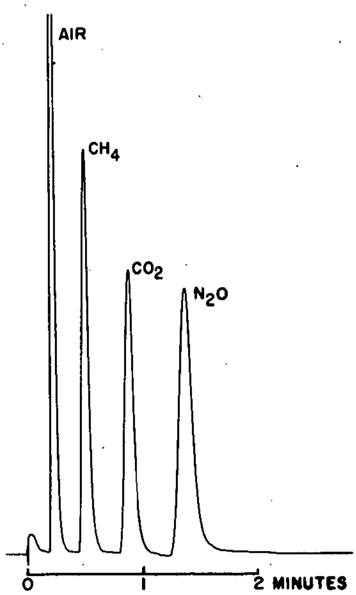

FIGURE 9 – Separation of Air, CH_4, CO_2 and N_2O.

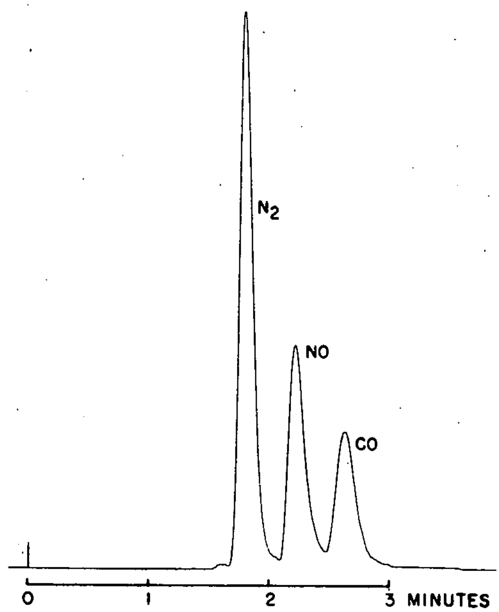

FIGURE 10 – Separation of N_2, NO and CO

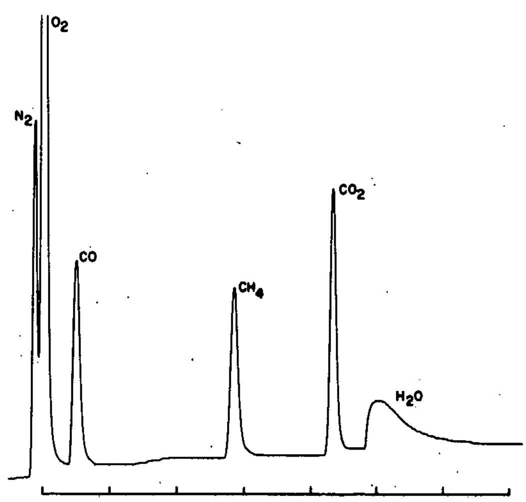

FIGURE 11 – Separation of O_2, N_2, CO, CH_4, CO_2 and H_2O.